

PROMISING CATALYSTS FOR H₂ - O₂ FUEL CELLS (REVIEW)

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Abstract. The aim of the present paper is to give the review of the recent investigations in the field of non-noble metal catalysts (group 1) and in the field of catalysts containing reduced amount of a noble metal due to the improvements in the technology of their preparation (group 2). Some novel electrocatalysts of oxygen reduction and hydrogen oxidation from both these groups are considered in this paper.

Keywords: electrocatalysts, oxygen reduction, hydrogen oxidation, fuel cells.

1. Introduction

The electrochemical storage of energy and its conversion are of great interest from the point of view of many practical applications. The market for portable fuel cells and batteries to electronic devices has recently strong tendency to expansion. Due to the requirements of environmental protection, a lot of research work is also devoted to the application of fuel cells and promising batteries in electrical vehicles. From the economical point of view and due to the requirements of the ecology there is a big demand for relatively low cost and environmentally friendly electrode materials and catalysts to be used for fuel cells and batteries. The decisive factors that must be taken into account when estimating the possibility of wide application of fuel cells are the cost and the effectiveness of the catalyst. The most important parts of fuel cells are electrocatalysts. They determine a cost and system capability of fuel cells. Mainly the noble metals (Pd, Pt) are used recently as anode and cathode catalysts in fuel cells. The most effective catalytic materials appear to be the materials prepared in the form of a thin layer of active catalyst precipitated at the surface of carbon, ceramic or other porous materials with a highly developed surface.

As fuel for fuel cells are used commonly hydrogen, methane, methanol, metal hydrides and other substances. Hydrogen has the highest weight specific energy (32,702 W·h/kg). The main types of hydrogen fuel cells are following:

1. Alkaline (AFC): These are used by NASA on the manned space missions, and operate well at about 80 °C. They use alkaline electrolyte, potassium hydroxide, and can generate electricity with the efficiency up to 70 %.
2. Proton Exchange Membrane (PEMFC): These cells use a perfluorinated ionomer polymer membrane which passes protons from the anode and cathode. They operate at about 80 °C. These are being developed for use in transport applications and for portable and small fuel cells.
3. Phosphoric Acid (PAFC): This is the most commonly used type of a fuel cell for stationary commercial sites like hospitals, hotels and office buildings. The cell operates at about 200 °C and shows the efficiency up to 85%.

- 4. Molten Carbonate (MCFC): These cells use a mixed alkali-carbonate molten salt electrolyte and operate at about 600 °C. They are being developed for continuously operating facilities, and can use coal-based or marine diesel fuels.
- 5. Solid Oxide (SOFC): These cells use a solid oxygen-ion-conducting metal oxide electrolyte. They operate at about 1000 °C, with an efficiency of up to 60%. They may find application in industrial and large-scale applications.

2. Results and Discussions

The catalytic properties of simple metals with respect to the system H₂-O₂ have been investigated experimentally for the long time in detail. Pt and Pd show the best catalytic activity (CA), as it is well known. The general theory of catalytic processes is developed rather poorly, as it is well known too. However, numerous experimental data point to a strong dependence of material CA on the processes of reagents adsorption and products desorption (Fig. 1) [1].

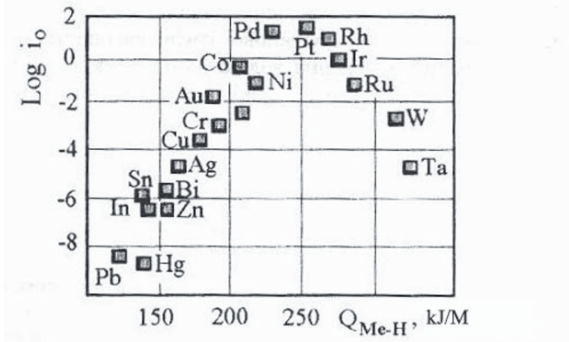


Figure 1. A correlation between the exchange current of hydrogen ion reduction and a bond energy (Q Me-H).

Some new catalysts for the reaction of the electrochemical hydrogen oxidation and oxygen reduction both from the groups 1 and 2 are presented below.

2.1. HYDROGEN OXIDATION CATALYSTS

The well - known anodic reactions of hydrogen oxidation in fuel cells are following:

- (1) $H_2 \rightarrow 2 H^+ + 2 e^-$ (in acid electrolyte)
- (2) $H_2 + 2 OH^- \rightarrow 2 H_2O + 2 e^-$ (in alkaline medium)

2.1.1 Non-noble metal catalyst (Table 1)

TABLE 1. Perspective non- precious metals catalysts for hydrogen oxidation

Catalyst	Method of preparation	Literature
Molybdenum carbide	gas-phase deposition	[3]
Tungsten carbide (WC)	- // - // - // -	[2, 3]
Radicals of following composition: -OH, -OSO ₃ H, -COOH, -OPO(OH) ₃	plasma treatment of gas diffusion layer	[4]
Allochromatium vinosum [NiFe]- hydrogenase	graphite supported adsorption Ni-Fe layer	[5]
Cr-Ni, La-Ni, Ti-Ni, Fe-Ni, Cu-Ni	deposition of respective metals on Raney nickel	[11]

New catalysts of hydrogen oxidation for low-temperature fuel cells are molybdenum and tungsten carbides [2, 3]. For solid polymeric fuel cells the novel catalysts by plasma treatment of polymer membrane have been developed. The radicals at surface are generated. These radicals are catalysts of anodic reactions [4] (Table 1).

Among the other metal catalysts for hydrogen oxidation, the *Raney nickel* deposited on the surface of graphite is widely known [10, 13]. The modification of Raney nickel with such metals like *Fe, Cr, Cu, La, Ti* has been proposed [11] with the aim to increase its effectiveness. The effectiveness of the doping metals follows the series: *Cr>La>Ti>Cu>Fe*.

2.1.2 Catalysts with the reduced noble metal content (Table 2)

To reduce the noble metals content in the electrode and to increase the catalyst activity, the electrode preparation by deposition of *Pd, Ni, Bi and La* on the surface of *Pt/C catalyst* [6], as well as the deposition of *Ru and Mo* on *platinum* by pulse electrodeposition at appropriate potentials have been elaborated [7].

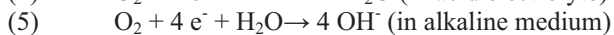
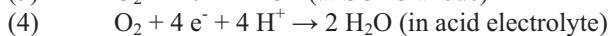
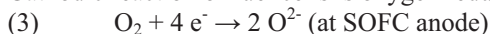
TABLE 2. Perspective noble metal catalysts for hydrogen oxidation

Catalyst	Method of preparation	Literature
Pt _x Ru _y and Pt _x Ru _y Mo _z	pulse electrolysis	[7]
Pd-Pt/C, Ni-Pt/C, Bi-Pt/C, La-Pt/C	deposition of Pd, Ni, Bi, La on the Pt/C catalyst	[6]
Cr-Ni, La-Ni, Ti-Ni, Fe-Ni, Cu-Ni	deposition of respective metals on Raney nickel	[11]
Pt-Pd/Au/C Pt-Ru/Au/C	deposition of sub-monolayers of Pt on Ru and Au nanoparticles supported by carbon materials	[12]
Pt/WO ₃ /C Pt-Ru/WO ₃ /C	Codeposition Pt and WO ₃ from solution by activated carbon	[28]

It is well-known that the presence of catalytic poisons (CO for example) in hydrogen gas exerts strong influence on the effectiveness and long-term stability of the electrodes containing Pt, Pd and other noble metals as a catalyst. The modification of this catalyst by such metals as Nb, Mo, Ta and Ru increased electrode life in presence of CO [8, 9]. Utilization of tungsten oxide (WO₃) jointly with Pt and Ru increase also electrode stability towards CO [28].

3. Oxygen reduction catalyst

Cathodic reaction of fuel cells is oxygen reduction.



The oxygen reduction begins on some step of reaction if pure catalyst is used. If catalysts are not good, the hydrogen peroxide is generated at some stages of electrode process. Hydrogen peroxide is very strong oxidizer and destroys the construction of the fuel cell. Therefore, the catalyst must provide four-electron mechanism of reaction. Such catalysts are showed in the Tables 3, 4.

3.1. NON-NOBLE METAL CATALYST (TABLE 3)

TABLE 3. Perspective non-precious metal catalysts for oxygen reduction

Catalyst	Method of preparation	Literature
Tungsten carbide (W_2C)	gas-phase deposition	[2, 3]
Co-polypyrrole complex	polypyrrole modification, deposited on carbon	[13]
Mixture of oxide Ni and Co	Vacuum deposition	[16]
Mn-polypyrrol-phthalocyanine complex	Electropolymerization	[14]
Co(II)-tetrasulphophtalo-phthalocyanine complex	Complex adsorption on SiO_2/TiO_2	[17]
$LaNi_{0.9}Fe_{0.1}O_3$, $La_{0.95}Sr_{0.05}Ni_{0.9}Fe_{0.1}O_3$	By ceramic technology	[19]
$La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ -CuO	- // - // - // -	[30]
MnO_x/C with ions Ca(II), Mg(II), Ni(II), Bi(III), Cr(III)	Reduction of $KMnO_4$ by carbon black	[15]

3.1.1. Conducting polymers (PANI, PPy and others as well as manganous oxides, perovskite and some other materials are used as non-noble metal catalysts.

Through examples of new catalyst of this class could be mentioned polymeric complexes such as Co-polypyrrole complex [13], Mn-polypyrrol-phthalocyanine complex [14], Co(II)-tetrasulphophtalophthalocyanine complex [17]. Active center of this catalyst is the metal ion encircled with nitrogen atoms. The structure of Mn-polypyrrol-phthalocyanine complex (MnTPhPyrPc) is showed in Fig. 2.

Modification by such ions like: Ca, Mg, Ni, Bi, Cr is proposed for improvement of manganous oxide catalyst [15]. The most effective modifiers are Ca(II) and Mg(II) ions.

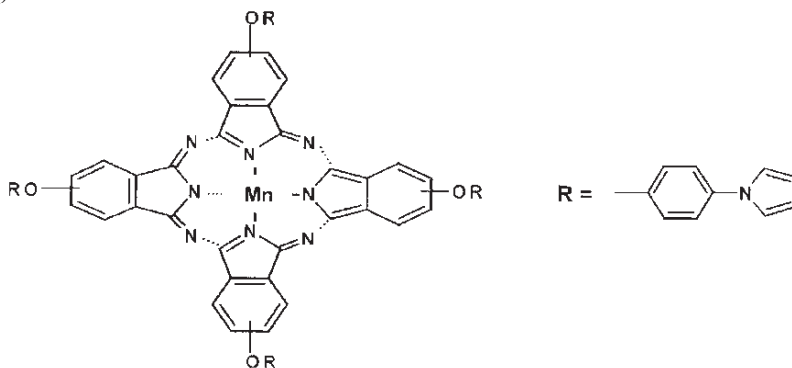


Figure 2. Structure MnTPhPyrPc.

3.1.2. Catalyst based on bioorganic substances

Interestingly that the bioorganic substances may be used in fuel cells as electrocatalysts. The new catalyst of hydrogen reactions is Allochromatium

vinosum [NiFe]–hydrogenase adsorbed on pyrolytic graphite [5]. Structure of Ni-Fe hydrogenase is showed in the Fig. 3. The effectiveness of this catalyst is comparable to the Pt catalyst.

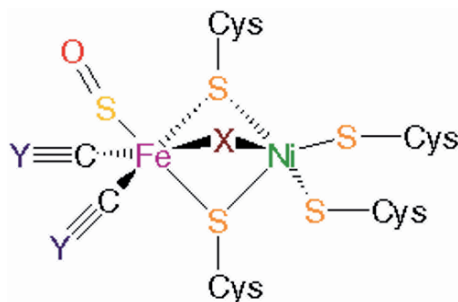


Figure 3. Structure Fe-Ni hydrogenase . X = S or O; Y = O or N; Cys = CYSTEINE.

The catalyst of oxygen reactions are derivatives of Vitamin B 12 [24]. These complexes contain an active sorption center, which consist of conjugated nitrogen atoms.

A mechanism of catalytic activity of electronically conducting polymers (ECP) of polyaniline (PANI) type was investigated in [26, 27]. To explain the reasons of the catalytic activity of ECPs, a quantum-chemical modeling of ECPs and adsorption complexes of ECPs with oxygen has been performed. The catalytic activity takes place due to the unique electronic structure of ECPs. The calculations showed that the bond orders in chemisorbed oxygen molecules at PANI decrease by one third, and the bond length increases by more than 20% in comparison with that in a free oxygen molecule. Thus, chemisorbed oxygen molecules have a fairly high degree of activation and can be readily reduced at the polymeric surface (Fig. 4). The similar mechanism takes place on the active carbon atoms of PPy, PT, PMeT.

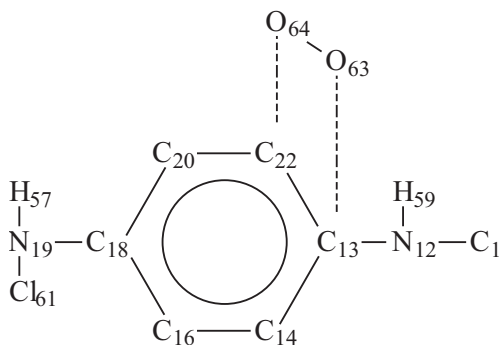


Figure 4. “Bridge model” of oxygen adsorption on PANI.

3.1.3. Catalysts with reduced content of the noble metal (Table 4)

Combinations of platinum catalyst and Fe-tetraphenylparapherine complex increased the efficiency of oxygen reduction [21]. The decay product of methanol in DMFC

decreased cathode efficiency for noble catalysts. Following catalysts are developed for DMFC: $\text{Os}_x(\text{CO})_n$ -Pt/C [28], CeO_2 -Pt/C [27], Fe-tetraphenylporphyrin- Pt/C [26].

TABLE 4. Perspective noble metal catalysts for oxygen reduction

Catalyst	Method of preparation	Literature
Deposition of derivative Vitamin B12 on Au	Spontaneous process on particles Au	[24]
Fe-tetraphenylporphyrine-Pt/C	–	[21]
CeO_2 -Pt/C	Deposition of CeO_2 on Pt/C	[22]
Pt-Ni/C, Pt-Co/C	Deposition Ni, Co, on Pt/C	[20]
$\text{Os}_x(\text{CO})_n$	Pyrolysis of $\text{Os}_x(\text{CO})_n$ at 180°C	[23]

4. Multi-functional catalysts

Interesting direction in the field of investigations of catalysts is the development of multi-functional catalysts that catalyse both the anodic hydrogen oxidation, as well as the cathodic oxygen reduction reactions. These catalysts are prepared mostly basing on noble metals. One of such catalysts is the material obtained by deposition of a monolayer of Pt on Pd and Au nanoparticles, deposited on the surface of high-purity carbon material [12]. Such catalyst increases the activity of electrode by 3-4 times in comparison with the commercial samples. The deposition of $\text{Pt}_{0.75}\text{Pd}_{0.25}$ monolayer on the gold particles distributed on carbon matrix allow to increase the catalytic activity of the oxygen reduction reaction 2.5 times in comparison with typical Pt catalyst.

The tungsten carbides (WC and W_2C) has also attracted attention. The WC is catalyst of hydrogen oxidation, the W_2C is catalyst of oxygen reduction. The technology of WC and W_2C preparation is identical.

The catalysts for oxygen reduction and oxygen oxidation are materials based on substances like Co, Ni, Fe, Mn [16, 19]. One of new applications of oxygen reduction catalysts is air-metal hydride accumulator. Electrodes based on $\text{La}_{0.1}\text{Ca}_{0.4}\text{CoO}_3$, $\text{La}_{0.1}\text{Ca}_{0.9}\text{MnO}_3$ [18] are used in this battery. The electrodes of similar composition could be used in SOFC. An insertion of the oxides in their composition (CuO for example) leads to increasing the conductivity of system and efficiency of catalyst [30].

5. Conclusions

It is possible to mark the following promising materials for the two main groups of catalysts:

Grope 1. Non-platinum catalysts:

For hydrogen oxidation: bi-component metal doped systems deposited on Raney nickel for AFC; Mo and W carbides for AFC prepared by method of precipitation from a gas phase; Radicals of following composition: $-\text{OH}$, $-\text{OSO}_3\text{H}$, $-\text{COOH}$, $-\text{OPO}(\text{OH})_3$ for PEMFC; Some organic catalysts like biologically active $[\text{NiFe}]$ -hydrogenase, pyropolymers, etc.;

For oxygen reduction: N4-organic metal complexes and conducting polymers, transition metals oxides, perovskites, etc.

Grope 2. Catalysts with reduced Pt, Pd content on carbon (ceramic) support:

For hydrogen oxidation: bi-component Pt-Me/C catalysts (with the best results for Pt-Pd/C); three-component Me-Pt-Pd/C catalysts (with the best results for Ni-Pt-Pd/C); Pt-Ru/C and Pt-Ru-Mo/C catalysts; Pt-Pd/Au/C and Pt-Ru/Au/C catalysts;

For oxygen reduction: composites of N₄-organic metal complexes and noble metal catalyst, bi-component Pt-Me/C (with the attained best result for Ni-Pt/C).

All above mentioned catalysts were developed taking into account the synergetic effects. That is why their further optimization needs finding the effective combination of different catalysts.

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